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## Short communication

# Evidence of acid–base interactions between amines and model indoor surfaces by ATR-FTIR spectroscopy

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**Abstract**

Molecular associations of pyridine with cellulose and gypsum, surrogates for common indoor surface materials, were studied using an attenuated total reflection (ATR)-Fourier transform infrared (FTIR) spectrophotometric method. The purpose of this study was to gain insight into the molecular interactions of amines with well-characterized materials that affect their partitioning between indoor air and surfaces. The experimental results suggest the presence of at least two sorptive states for volatile and semivolatile amines, attributed to the chemisorbed species and to a more labile surface state (i.e., physisorbed pyridine). Both exhibited spectroscopic signatures corresponding to aromatic C–H stretching modes ( $2950\text{--}3100\text{ cm}^{-1}$ ) in the studied spectral region. Chemisorbed pyridine could be identified by the presence of additional IR signals in the N–H and O–H stretching region of the spectrum ( $2900\text{--}3600\text{ cm}^{-1}$ ). During desorption under a stream of  $\text{N}_2$ , surface enrichment in the chemisorbed species was evidenced by a slower reduction of the absorbance of the broad band at  $2900\text{--}3600\text{ cm}^{-1}$  in relation to the total pyridine absorbance change. This spectroscopic evidence for acid–base interactions between amines and surfaces is consistent with the desorption behavior observed in previous work for nicotine from model surfaces.

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**Keywords:** Acid–base; Nicotine; Pyridine; Sorption; Gypsum; Cellulose; Surface materials**1. Introduction**

The extent to which volatile and semivolatile organic chemicals adhere and remain associated with indoor materials varies widely, depending on their vapor pressure and molecular interactions with surfaces sites (Goss, 1997; Singer et al., 2004). Evaluation of acid–base surface association processes is critical to the understanding of the indoor

dynamics of amines emitted from tobacco smoking and other indoor pollution sources, and the hydrolysis of phthalate ester plasticizers, among other indoor pollutants (Weschler, 2004). Webb et al. (2002) found that the presence of gaseous  $\text{NH}_3$  in indoor air increased the desorption rate of nicotine sorbed to walls, carpet and furnishings, and inferred that this observation was related to the influence of acid–base chemistry on the nicotine sorption/desorption processes. In a recent study, Ongwande et al. (2005) demonstrated that the sorptive capacity of trimethylamine on mineral surfaces increased by

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40–50% when the CO<sub>2</sub> mixing ratio increased to 1000 ppm and was reduced by ~5–80% due to competition with NH<sub>3</sub> for ammonia levels in the order of 10 ppm and relative humidity in the range RH = 20–90%. Those effects are also attributable to acid–base surface interactions of the amine.

In this work, we evaluated attenuated total reflection (ATR)-Fourier transform infrared (FTIR) spectroscopy as a tool to explore acid–base interactions between amines and model surface materials and their impact on sorption and desorption. Infrared spectra of sorbed pyridine are commonly used as a probe for acidic surface sites in catalysts (Ferreto and Glisenti, 2002; Iordan et al., 2004). Pyridine also has relevance as a member of a group of basic compounds in tobacco smoke, including nicotine and substituted pyridines. We selected simple surfaces that are representative of various chemical functionalities present in common indoor materials. Cellulose is a glucose polysaccharide that is the principal component of the paper used in wallboard panels and wallpaper, as well as in cotton and other fabrics used in indoor furnishings. Gypsum is the main constituent of the core of wallboard panels.

## 2. Experimental

FTIR spectra were measured with a Nicolet Magna 760 spectrophotometer provided with a PbSe detector operating in the range 5000–2000 cm<sup>-1</sup> and a XT-KBr beamsplitter. Spectra of gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O) and cellulose films, spectra of pure pyridine and those of pyridine sorbed to gypsum or cellulose films were collected using an ATR crystal, following a modification of the method described by Sayer and Horn (2003). A thin layer of each sorbent material was obtained by applying 1–2 mL of a slurry over the surface of a ZnSe ATR crystal (4.06 cm<sup>2</sup>) and allowing for complete evaporation of the solvent. The slurry was prepared by suspension of fine powders (<100–125 mesh) of each sorbent material in acetonitrile. Solvent evaporation was accelerated by applying a gentle N<sub>2</sub> stream (0.2–1 L min<sup>-1</sup>), and was monitored following the disappearance of the C≡N stretching band at 2220 cm<sup>-1</sup>. In separate experiments, pure pyridine spectra were obtained by directly introducing a layer of the liquid on the surface of the crystal.

In order to obtain samples with pyridine sorbed to gypsum or cellulose powders, the slurries were

prepared using a solution of 10% pyridine in acetonitrile, and the solvent was evaporated as described above. After evaporation of the solvent, further application of the N<sub>2</sub> stream accelerated desorption of pyridine from the films over the course of 22 or 50 min (for pyridine–cellulose samples and pyridine–gypsum samples, respectively). The N<sub>2</sub> atmosphere also prevented the uptake of moisture from surrounding air during solvent evaporation and pyridine desorption.

Once the evaporation of acetonitrile was complete, spectra in the range 5000–2000 cm<sup>-1</sup> were recorded at ~2 min intervals until pyridine was substantially desorbed. Gravimetric measurements performed after pyridine desorption in each experiment indicated that 19–36 mg of dry sorbent material deposited, corresponding to film thickness between 20 and 38 μm. Such film thickness is significantly greater than the penetration depth of the infrared beam. For the considered wavelength range and at our experimental incidence angle of 40°, the effective penetration depth into the sample was 0.5–1.0 μm. We determined the N<sub>2</sub>-BET surface areas of gypsum and cellulose powders as 17.2 and 1.79 m<sup>2</sup> g<sup>-1</sup>, respectively, using a Micromeritics TriStar 3000 Gas Adsorption Analyzer. Total surface area in our samples was in the range 0.03–0.6 m<sup>2</sup>, corresponding to a maximum pyridine surface concentration of 1.5–60 mmol m<sup>-2</sup>. In fact, pyridine surface concentrations were significantly lower than those values, due to evaporation during solvent removal.

## 3. Results and discussion

Fig. 1 shows spectra obtained when pure gypsum was deposited on the ATR crystal (A), when pure pyridine was applied on the crystal (B) and when pyridine was adsorbed on the gypsum film following the method described in the experimental section (C). In the first case, no significant bands were observed in the studied spectral range. For pure pyridine, there was a cluster of narrow bands between 2950 and 3100 cm<sup>-1</sup> corresponding to aromatic C–H stretching. When pyridine was sorbed to gypsum or cellulose, the spectral signature corresponding to C–H stretching (2950–3100 cm<sup>-1</sup>) was preserved, and an additional broad band was observed at higher energies, in the range 3000–3600 cm<sup>-1</sup>. That new signal (observed with both gypsum and cellulose substrates) can be attributed to N···H and/or to O–H stretching



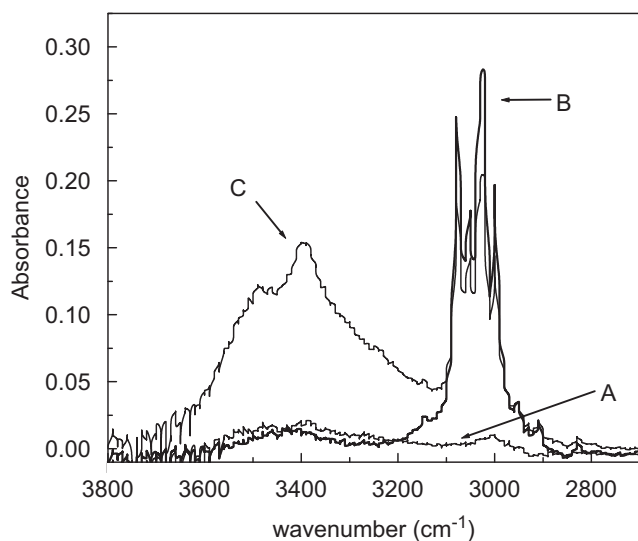


Fig. 1. ATR-FTIR spectra of pure gypsum (A), pure pyridine (B) and of pyridine sorbed on gypsum (C).

resulting from hydrogen bonding between the amine and OH surface groups. Those OH groups are present in the molecular structure of cellulose and in structural water molecules in gypsum, and could be considered Brønsted-type acidic surface sites.

We analyzed the relative lability of pyridine adsorbed to different surface sites by following the intensity changes of the main spectral signatures during desorption of the amine under a nitrogen stream. Fig. 2 shows absorbance values measured for the C–H and hydrogen-bonded peaks (values on the left axis), and the absorbance ratio between chemisorbed and total pyridine, corresponding to (NH+OH)/CH stretching bands (values on the right axes), as a function of desorption time. Assuming that the C–H stretching signal (measured at 3025 cm<sup>-1</sup> for both substrates) was a good indicator for “total pyridine”, the desorption rate corresponding to pyridine that is associated to the substrate through hydrogen-bond (measured at 3390 and 3500 cm<sup>-1</sup> for pyridine–gypsum and at 3340 cm<sup>-1</sup> for pyridine–cellulose) was slower than for the physisorbed molecule. This observation suggests the presence of two distinct sorptive states of the amine: a labile, physisorbed state and a stronger association through acid–base interactions.

### 3.1. Amine–surface interactions and desorption dynamics

Complementary evidence of the presence of more than one sorptive state in the interaction of amines with model surfaces can be gleaned from (non-

spectroscopic) chamber desorption experiments. In a recent study performed in a 200-L chamber with internal Teflon surfaces (Destailats et al., 2006), we recorded the gas-phase concentration of nicotine during its desorption from chamber walls under a constant flow of dry air with an air change rate of 1.5 h<sup>-1</sup>. Initial nicotine concentrations were 10–15 µg L<sup>-1</sup>. Two conditions were analyzed: only Teflon surfaces vs. a combination of cotton and Teflon surfaces. In the latter, only ~1/6 of the chamber walls were covered with a cotton cloth (details on the experimental conditions are provided in the original article). Nicotine sorbed to a much larger extent to the cotton and therefore re-emission levels during desorption were roughly one order of magnitude higher than in Teflon-only experiments. Fig. 3 shows the nicotine desorption profiles determined in Teflon-only tests (Fig. 3a) and from cotton surfaces (Fig. 3b).

In both cases, the gas-phase concentrations initially decreased at approximately the ventilation removal rate (non-sorptive behavior). The desorption phase of the experiments can be modeled using a set of differential equations that describe a time-dependent mass balance for nicotine in the gas phase (concentration  $C$  in mol m<sup>-3</sup>) and sorbed in  $i$  different sorptive states or surface sinks, with a surface concentration of  $S_i$  in each of them, expressed in mol m<sup>-2</sup>. The analytical solution yields a general expression for nicotine gas-phase concentration  $C$  as a function of time that can be used to fit the experimental data:

$$C(t) = C_0 \exp(-\lambda t) + \sum_i \frac{A}{V} \frac{k_i}{(\lambda - k_i)} \times S_{i,0} \{ \exp(-k_i t) - \exp(-\lambda t) \}, \quad (1)$$

where  $\lambda$  is the air exchange rate (in min<sup>-1</sup>),  $A$  and  $V$  are the chamber area and volume, respectively, and  $k_i$  is the desorption rate corresponding to the  $i$ th surface species (in min<sup>-1</sup>). Eq. (1) assumes that adsorption rates for each sink are much slower than air exchange rates. The parameters  $\lambda$  and  $C_0$  can be measured experimentally. We fitted Eq. (1) (for  $i = 1$  and 2) to the data points shown in Figs. 3a and 3b using a least-squares method to obtain the best fits for  $k_i$ , and for  $S_{i,0}' = S_{i,0} (A/V)$ , an equivalent initial surface concentration. The fitted curves are shown in Fig. 3, together with the experimental values. The single-sink model provided a relatively good fit for nicotine desorption from Teflon surfaces and the fit was not significantly improved



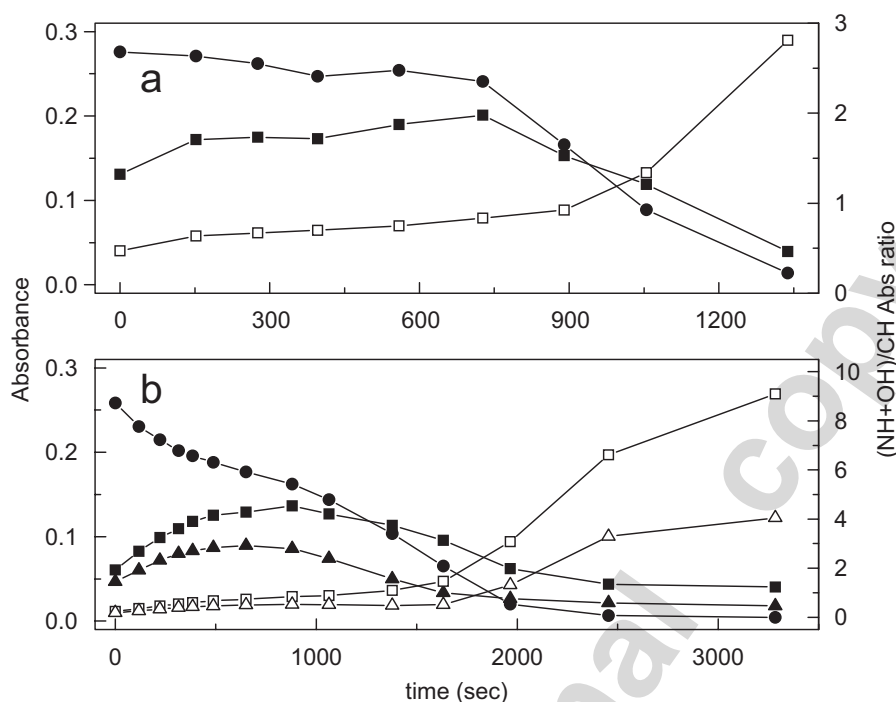


Fig. 2. Desorption of pyridine from cellulose (a) and gypsum (b) films. Infrared absorbance (left axis) of C–H bands at  $3025\text{ cm}^{-1}$  (●), (N···H+O–H) bands at (a)  $3340\text{ cm}^{-1}$  (■); (b)  $3390\text{ cm}^{-1}$  (■) and  $3500\text{ cm}^{-1}$  (▲). Abs ratios (N···H+O–H)/C–H ( $\Delta$ ,  $\square$ ) shown on the right axis.

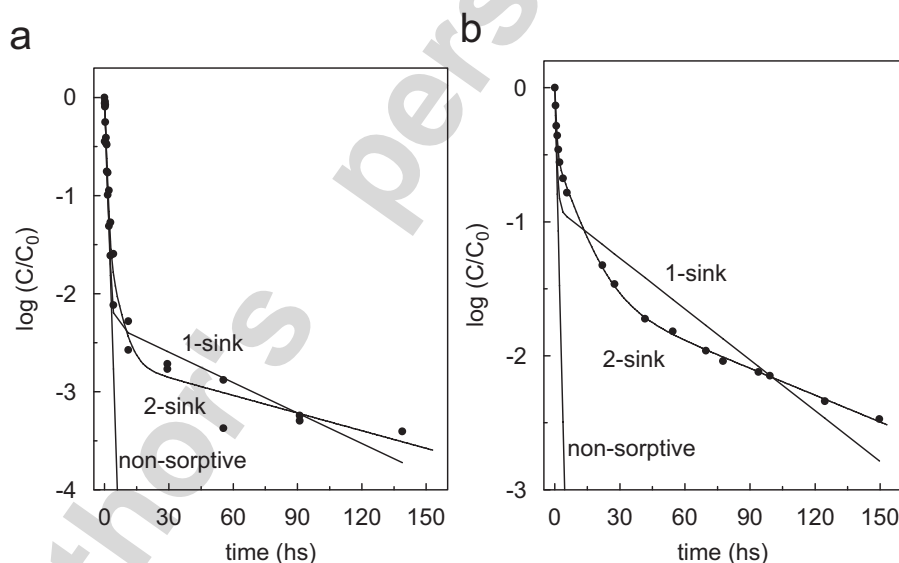


Fig. 3. Desorption of nicotine from (a) Teflon surfaces, and (b) a cotton cloth. Experimental data (●) are shown with curves corresponding to 1-sink model, 2-sink model and non-sorptive ideal behavior.

by addition of another sink. In contrast, the two-sink model was needed to reproduce experimental results with cotton, a surface where acid–base interactions with amines are likely predominant. This observation suggests that two different sorptive states having differing desorption rates are present in the nicotine–cotton system, but not in the nicotine–Teflon system. This outcome is consistent

with the spectroscopic analysis for pyridine on gypsum and cellulose.

#### 4. Conclusion

Modeling of indoor sorption and desorption of organic pollutants usually involves the definition of two different surface compartments: a “fast” and a



“slow” reservoir or sink, from which compounds are allowed to desorb at different rates (Piade et al., 1999; Singer et al., 2004). Those two sinks may represent a variety of chemical and physical phenomena taking place on material surfaces, comprising not only the chemical diversity of surfaces exposed to indoor air, but also the possible presence of “embedded” or less accessible sinks. Our results indicate that, even for very simple surfaces, volatile and semivolatile amines may exhibit desorption behavior involving more than one surface state, as a consequence of acid-base and other strong chemical interactions with surface sites.

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